5.3 Excessive moisture in the sample matrix can generate negative bias in the analytical results. Decreased sample size and increased drying agent must be utilized to compensate for excessive moisture content.

5.4 When the volume of the solvent is reduced below 1 ml, semi-volatile analytes may be lost. Care must be taken when reducing volume to 1 ml.

5.5 Never allow the solvent level to go dry. If the solvent goes dry, the extraction process must be repeated.

6) Interferences

6.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organo-chlorine pesticides may de-chlorinate, phthalate esters may exchange, and phenols may react to form tannates.

6.2 Method interference may be caused by contaminants in solvents, reagents, glassware, and sample processing hardware. This contaminates lead to discrete artifacts or to elevated baselines in gas chromatograms. These materials must be routinely demonstrated to be free from interference under the sample preparation and analysis conditions by analyzing instrument and method blanks.

6.3 Interference caused by phthalate esters can pose a major problem in pesticide analysis. Because common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, cross-contamination of glassware frequently occurs when plastics are handled. Interference from phthalates is minimized when the use of plastic materials is avoided.

6.4 Matrix interference may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures in this method may be used to remove interference in order to achieve the Practical Quantitation Limit (PQL).

7) Personnel Qualifications and Responsibilities

7.1 Each analyst must be trained, read and understand the method, read and understand the SOP, and prepare acceptable initial demonstration samples to establish method competency for this analysis.

7.2 It is the responsibility of the analyst(s) to:

7.2.1 Follow this SOP as written. Any deviations or nonconformance must be documented and submitted to the department supervisor for signature.
7.2.2 Produce contractually compliant data that meets all quality requirements using this procedure.
7.2.3 Complete the required demonstration of proficiency before performing this procedure without supervision.

7.3 Department Supervisor: It is the responsibility of the department supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have adequate training required to perform this procedure.
7.3.2 Ensure analysts have completed the required demonstration of proficiency before performing this procedure without supervision.
7.3.3 Approve any required deviations and nonconformance incorporated into final

reports.

7.4 QA Manager: The QA Manager is responsible for:

7.4.1 Ensuring that the analytical method and SOP are followed as written through internal method and systems audits.

7.5 Project Manager: It is the responsibility of the project manager to ensure that all contractual requirements for a client requiring this procedure are understood prior to initiating this procedure for a given set of samples.

8) Sample Collection, Handling, and Preservation

8.1

SEMIVOLATILE ORGANICS, DIESEL/OIL RANGE ORGANICS, AND ORGANOCHLORINE PESTICIDES			
Sample Matrix	Container	Preservative	Holding Time
Solid Samples	250-mL widemouth glass container with Teflon-lined lid	Cool to 4°C	Extraction 14 days/Analysis 40 days
POLYCHLORINATED BYPHENOLS (PCBs)			
Solid Samples	250-mL widemouth glass container with Teflon-lined lid	Cool to 4°C	Extraction 365 days/Analysis 40 days

9) Equipment and Supplies

9.1 Microwave Reaction System capable of performing the required temperature and pressure parameters described in EPA Method 3546. CEM MARS or equivalent

9.2 Extraction Vessels, PFA with 60 mL capacity, screw cap with built in pressure release- MARS Express, or equivalent.

9.3 Manual Torque Tool - CEM part #185245 or equivalent

9.4 Glass funnel, 75mm diameter and 1-3 inch stem.

9.5 Vials- Glass, 2-mL capacity with Teflon caps.

9.6 Vials- glass, 12 mL and 40 mL (VOC) capacity, with Teflon lined screw tops.

9.7 Disposable glass pipettes

9.8 Top loading balance-capable of weighing to 0.01 g (for sample weight measurements).

9.9 Metal Spatulas

9.10 Syringes, various sizes-3mL, 1000ul, etc.

9.11 Graduated Cylinders, various sizes, Class A Glass

9.12 Kuderna Danish concentration apparatus

9.13 N-Vap Evaporation Unit, maintaining temperature <40*C

9.14 TurboVap Concentration Unit and Tubes.

9.15 Filter Paper, 15cm glass fiber, VWR or equivalent

9.16 Kimwipes

10) Standards and Reagents

10.1 HPLC, Pesticide, and other such high purity solvents shall be used for all tests. Reagent grade inorganic chemicals shall be used. Unless otherwise indicated, it is intended that all reagents shall confirm to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

10.2 Hydro-matrix: (Available from Agilent and/or Dionex.) Prior to use, purify by heating at 400° C. for four hours in a muffle furnace using a shallow Pyrex tray.

10.3 Sodium Sulfate (granular, anhydrous), Na2SO4. Purify by heating at 400 °C for four hours in a shallow tray, or by pre-cleaning with methylene chloride. If pre-cleaned with methylene chloride, a method blank must be analyzed, demonstrating the absence of interference. Document the preparation of sodium sulfate and assign a new code to the prepared reagent for use in sample preparation.

10.4 Soil/sediment and aqueous sludge samples are extracted using the following solvents systems:

Table 10.4 - Method Extraction Solvent Systems

Determinative Method	Extraction Solvent	Exchange Solvent
Organochlorine Pesticides, PCBs, DRO/ORO, PNAs (8081A, 8082, 8015, and 8270)	Hexane	None
Semi-volatile Organics (8270)	Methylene Chloride	None

10.5 Spiking Solutions:

10.5.1 PCB Surrogate Spike @ 1 ug/ml
10.5.2 PCB Matrix Spike @ 5 ug/ml
10.5.3 Pesticide Surrogate Spike @ 1 ug/ml
10.5.4 Pesticide Matrix Spike @ 1 ug/ml
10.5.5 Semi-Volatile Surrogate @ 100 ug/ml
10.5.6 Semi-Volatile Matrix Spike @ 40 ug/ml
10.5.7 PNA Surrogate Spike @ 100 ug/ml
10.5.8 PNA Matrix Spike @ 40 ug/ml
10.5.9 DRO-ORO Matrix Spike @ 50,000 ug/ml

10.6 Reagent Storage:

10.6.1 Spiking solutions are prepared as needed from stock standards according to the applicable SOP.
10.6.2 Solutions must be stored refrigerated and protected from light.
10.6.3 Stock standards must be replaced after 1 year or according to manufacturer's

direction.

10.6.4 Prepared intermediate standards must be replaced every 6 months or sooner if a component degrades sooner.

10.7 Reagent Preparation Records

10.7.1 Record all stock standards in the Chemical inventory Logbook

10.7.2 Record all standards prepared in the Standard Preparation Logbook according to SOP HN-QS-001.

10.7.3 Label standards appropriately to ensure traceability. Labeling must include BPL number, date of expiration, name, and concentration.

11) Method Calibration

11.1 Perform support equipment calibration checks as required for daily use.

12) Sample Preparation/Analysis

12.1 The decision to use this extraction technique shall be based on the ability of the drying agent to effectively dry 15 grams of sample. If excessive moisture is present in the sample or if a non-aqueous layer is present in the sample, an alternative extraction technique, i.e. Sonication or Soxhlet extraction shall be employed.

12.2 Discard and decant any water layer on a sediment sample. Discard any foreign objects such as sticks, leaves, and rocks. Mix as necessary so that a representative sample can be withdrawn. This is best achieved by either mixing the material in the container using a disposable spatula, or by removing the entire contents to a mixing dish and thoroughly mixing. After mixing, remove an appropriate portion for sample preparation.

12.3 Waste Samples

12.3.1 Samples consisting of multiple phases must be prepared by the phase separation method. This extraction procedure is for solids only.

12.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of drying agent to the sample (1:1) may make the mixture amenable to grinding.

12.5 Microwave Extraction:

12.5.1 Rinse all glassware and extraction vessels with appropriate solvents before use.

12.5.2 All QC must be handled in the same manner as samples, including the addition of drying agents and mixing in intermediate vessels.

12.5.3 Sample Preparation:

12.5.3.1 PCBs, Pesticides, DRO/ORO, and PAHs

12.5.3.1.1 Sample Size:

12.5.3.1.1.1 With a metal spatula, weigh (to the nearest 0.01g) a 15.00g well-mixed portion of sample into a PFE mixing cup.

12.5.3.1.1.2 For extremely lightweight or high moisture samples, a lesser weight may be used.

12.5.3.1.2 Record the actual weight in the preparation log.

12.5.3.1.3 Mix with sufficient drying agent to generate a free flowing matrix. This step is critical to the extraction process.

12.5.3.1.4 Using a powder funnel, transfer the entire sample to a microwave extraction vessel.

12.5.3.1.5 Clean the threads of the extraction vessel with a Kimwipe to ensure no particulates have accumulated, which would prevent a proper seal on the vessel.

12.5.3.1.6 Proceed to Section 12.5.5

12.5.3.2 SVOA

12.5.3.2.1 Sample Size:

12.5.3.2.1.1 With a metal spatula, weigh (to the nearest 0.01g) a 15.00g well-mixed portion of sample into a PFE mixing cup.

12.5.3.2.1.2 For extremely lightweight or high moisture samples, a lesser weight may be used.

12.5.3.2.2 Record the actual weight in the preparation log.

12.5.3.2.3 Mix with sufficient drying agent to generate a free flowing matrix. This step is critical to the extraction process.

12.5.3.2.4 Using a powder funnel, transfer the entire sample to a microwave extraction vessel.

12.5.3.2.5 Clean the threads of the extraction vessel with a Kimwipe to ensure no particulates have accumulated, which would prevent a proper seal on the vessel.

12.5.3.2.6 Proceed to Section 12.5.5

12.5.4 Samples requiring quick turn-around may not have percent moisture calculations completed prior to commencing extraction. In such cases, the analyst should base sample size upon their professional judgment keeping in mind that moisture control is critical.

12.5.5 Identify the sample contained in each vessel.

12.5.6 Spike all client and QC samples with appropriate Surrogates and Spikes (Table 22.4).

12.5.7 Using a graduated cylinder, add 25 mL of the appropriate extraction solvent (Table 10.4) to each vessel.

12.5.8 Re-check the threading of the vessel and cap to ensure no particulate has

deposited.

12.5.9 Screw the cap on the vessel and ensure it is on tight utilizing the manual torque tool.

12.5.10 Invert and shake the vessels several times until the solvent reaches the bottom of the cell and is well mixed with the sample. It is critical that the solvent be well mixed to ensure even heating of the sample and solvent.

12.5.11 Arrange sample vessels in the turnstile according to manufacturer specifications, using the vessel map in section 22.5 of this SOP, so to balance the extraction vessels throughout the turnstile. Record the location of each sample in the turnstile.

12.5.11.1 Note: an even number, no less than 8, vessels must be placed into the turnstile. Utilize additional blank vessels to ensure that appropriate positions are filled.

12.5.12 Turn on the fume hood and ensure that the exhaust line is routed into the hood.

12.5.13 Method Selection:

12.5.13.1 One Touch Method "USEPA 3546 - 115C"
12.5.13.2 Ramp Time to Hold: 15-20 min.
12.5.13.3 Hold Time: 15 min.
12.5.13.4 Hold Temperature: 115°C
12.5.13.5 Power: 1030-1800 watts
12.5.13.6 Cooling Time: 30 min. or until at room temp

12.5.14 The unit must be monitored to ensure each batch meets the method requirement of reaching a temperature of 115°C and holding at that temperature for a minimum of 10 minutes. Failure to reach and hold the batch at 115°C for 10 minutes requires rejection of the samples. Venting of the cells as indicated by the solvent sensor due to excess pressure, will automatically terminate the program and warrant the re-extraction of samples. A modification in ramp time and adjustments in power outputs are acceptable as long as the sample reaches 115°C and holds for a minimum of 10 minutes.

12.5.15 Once samples are cool to touch, transfer the solvent from the extraction vessel into the appropriate concentration device (12.5.16) using a pre-rinsed funnel and filter paper. Use additional aliquots of extraction solvent as a rinse to ensure a quantitative transfer of the extraction solvent to the concentration device. **Alternatively, an aliquot of the extract can be delivered to the instrument lab without concentration, for analysis by large volume injection (PNA, DRO/ORO, PCB, PEST).**

12.5.16 If solvent concentration is utilized, SVOA samples are transferred to a 250 mL K-D setup equipped with a 10 mL concentration tube and a 3-ball snyder column. Add a boiling chip prior to system closure. Other types of samples are transferred to a Turbo Vap Tube for concentration.

12.6 K-D Concentration Technique:

12.6.1 Place K-D setup in the hot water bath. Water bath must be in a hood or have a solvent recovery system attachment.

12.6.2 Concentrate the sample to approximately 10 ml. Ensure that the water bath is maintained at a temperature of 70° C when concentrating methylene chloride.

12.6.3 Remove K-D assembly from water bath and cool.

12.6.4 Prior to removing concentration tube, carefully wipe the connecting joint with a Chem-Wipe and visually inspect to ensure the absence of any water.

12.6.5 Carefully remove the concentrator tube and transfer to the N-Vap Blow Down Unit.

12.7 N-Vap Blow Down

12.7.1 Blow down sample to approximately 0.75ml with gentle stream of nitrogen.

12.7.2 Quantitatively transfer to an appropriately labeled vial and bring to a final volume of 1.0 ml with methylene chloride.

12.7.3 Transfer the finalized extracts to the appropriate analytical section for storage and/or analysis.

12.8 Turbo Vap™ Blow Down

12.8.1 Blow down to approximately 3.0 mL and quantitatively transfer to an appropriately labeled vial.

12.8.2 Bring to a final volume of 5.0 mL with Hexane.

13) Troubleshooting

13.1 Refer to CEM MARS 6™ technical manual.

14) Data Acquisition

14.1 Sample preparation information is logged into LIMS by prep batch with associated pertinent information.

14.2 All consumable items used in the extraction process must be documented in a manner yielding them traceable to the samples for which they were used.

14.3 This information is linked to the pertinent analytical method and associated results.

15) Calculation, and Data Reduction Requirements

15.1 See the determinative SOP for applicable calculations.

16) Quality Control, Data Assessment and Corrective Action

16.1 Method Blank

16.1.1 Frequency

16.1.1.1 One per batch of sample digestions (every 20 or less commercial samples extracted in the same 8 hour working shift)

16.1.2 Criteria

16.1.2.1 See the applicable determinative SOP

16.2 Laboratory Control Samples (LCS)

16.2.1 Frequency:

16.2.1.1 One per batch of 20 or less sample extractions.

16.2.2 Criteria

16.2.2.1 See the applicable determinative SOP

16.3 Matrix Spikes (MS/MSD)

16.3.1 Frequency

16.3.1.1 Matrix Spikes will be analyzed on a frequency of matrix spike pair for each preparative batch of 20 or less.

16.3.2 Criteria

16.3.2.1 See the applicable determinative SOP

16.4 Surrogate Standards must be added to all samples and QC samples.

16.5 For more complete information on data assessment and corrective action, refer to each determinative method SOP. The analyst will make the primary decisions concerning assessment and correction action.

17) Data Records Management

17.1 Document each sample prep batch into the Extractions Prep Logbook completing each requested item. If an item is not applicable then line through that section. No blank spaces should be left in the logbook. Uncompleted sections may be "Z'd" or "X'd" and then initialed.

17.2 All reagents and chemicals purchased and/or prepared must be labeled and traceable back to the respective chemical inventory and reagent/standard preparation logbooks. Make sure that all reagents have a tracking number. Log all reagents and chemicals used into the Extractions Prep Logbook. Make sure all reagents, chemicals and standards are dated.

17.3 All records must be maintained for a period of no less than 10 years.

18) Quality Assurance and Quality Control

18.1 Logbooks must be reviewed monthly by the department supervisor.

18.2 Logbooks must be reviewed quarterly by the QA Staff.

18.3 Internal audits are performed by the QA Staff on a periodic basis to ensure compliance with the procedures outlined in this SOP.

19) Contingencies for Handling Out of Control Data

19.1 Handling Out of Control Data:

19.1.1 Ideally, data should never be reported when the associated QC data fail criteria.

19.1.2 Should sample re-preparations and re-analysis be an impossibility, or method required corrective actions be an inadequate for the reporting of the data, the data can only be reported with the use of appropriate data qualifiers and project narration.

19.2 Deviations from this SOP or the acceptance criteria outlined within must be documented via the NC/CA database.

20) Method Performance

20.1 MDL studies are performed on an annual basis and whenever major method modifications occur.

21) Summary of Changes

Table 21.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
R01	12/1/15	CES	New SOP
R02	2/1/17	CES	Added Section 22.5, vessel distribution guide. Added LVI no concentration option.
R03	6/6/17	CES	Updated table 10.4 to represent Hexane only extraction.

22) References and Related Documents

22.1 U.S. Environmental Protection Agency, "Method 3500C (Revision 3, November 2000) Organic Extraction and Sample Preparation", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Update IV, November 27, 2000.

22.2 U.S. Environmental Protection Agency, "Method 3546, Microwave Extraction", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Update IV, February, 2007

22.3 ALS Environmental Quality Assurance Manual, Revision (most current)

22.4 Surrogate & Analyte Spike Additions (Table 22.4)

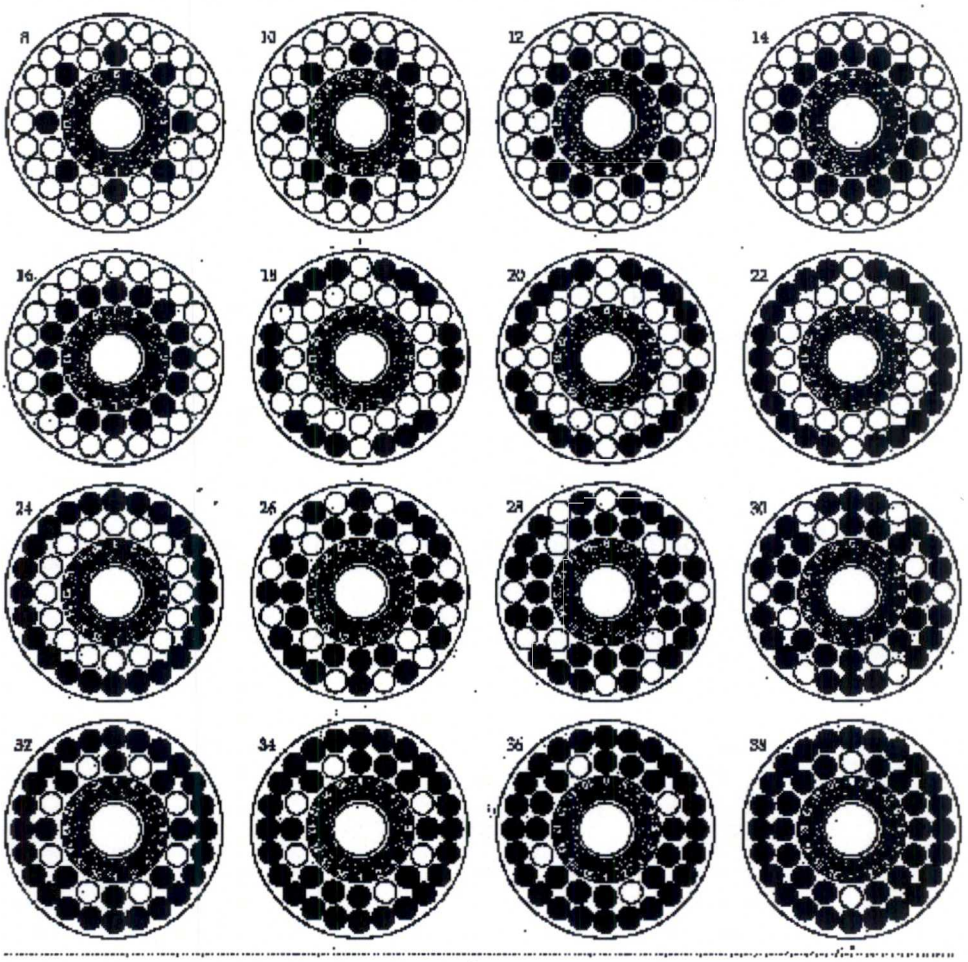
22.5 Vessel Distribution Guide

Table 22.4 - Surrogate & Analyte Spike Additions

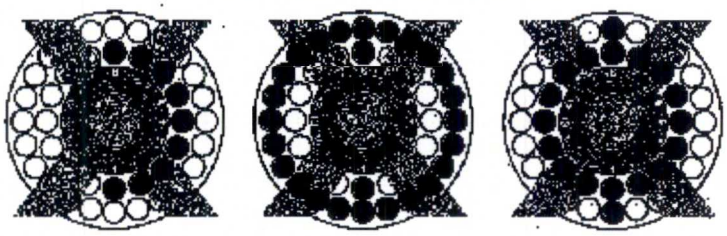
Analysis	*Final Volume* LVI / STD	*Surrogate Addition*	*Spike Addition*
PCBs	25 ml / 5 ml	0.5 ml @ 1 ug/ml	2.5 ml @ 5 ug/ml
Pesticides	25 ml / 5 ml	0.5 ml @ 1 ug/ml	0.5 ml @ 1 ug/ml
PAH/SVOA	25 ml / 1 ml	0.5 ml @ 100 ug/ml	0.5 ml @ 40 ug/ml
DRO/ORO	25 ml / 1 ml	0.5 ml @ 100 ug/ml	100 ul @ 50 mg/ml

22.5 – Vessel Distribution Guide

Recommended distribution of MARSXpress vessels when turntable is less than capacity



Incorrect distribution: What not to do



ORGANOCHLORINE PESTICIDES

SW846 8081A / 8081B / EPA 608.3

SOPID:	HN-GC-001	Rev. Number:	R06	Effective Date:	10/31/2017

Approved By: _____ Date: 10/19/17
Department Supervisor – Rob Swick

Approved By: _____ Date: 10/19/17
Laboratory Director – Jeff Glaser

Prepared By: _____ Date: 10/19/17
QA Manager – Chad Stoike

Archival Date: _____ Doc Control ID#: _____ Editor: _____

PROCEDURAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR 24 ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

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ORGANOCHLORINE PESTICIDES

1) Scope and Applicability

1.1 This Standard Operating Procedure is used to determine the concentrations of various organochlorine pesticides in extracts from solid and liquid matrices utilizing a gas chromatograph equipped with electron capture detectors (ECD). This procedure references SW-846 Method 8081A, 8081B, and EPA 608.3.

Compound	CAS Registry No	Compound	CAS Registry No
4,4'-DDD	72-54-8	Endosulfan I	959-98-8
4,4'-DDE	72-55-9	Endosulfan II	33213-65-9
4,4'-DDT	50-29-3	Endosulfan sulfate	1031-07-8
Aldrin	309-00-2	Endrin	72-20-8
α-BHC	319-84-6	Endrin aldehyde	7421-93-4
β-BHC	319-85-7	Endrin ketone	53494-70-5
γ-BHC (Lindane)	58-89-9	Heptachlor	76-44-8
δ-BHC	319-86-8	Heptachlor epoxide	1024-57-3
α-Chlordane	5103-71-9	Methoxychlor	72-43-5
γ-Chlordane	5103-74-2	Toxaphene	8001-35-2
Dieldrin	60-57-1	Chlordane, Technical	12789-03-6

1.2 This SOP describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column.

1.3 This SOP includes a dual-column that allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual-column analysis.

2) Summary of Procedure

2.1 A measured volume or weight of sample (approximately 125mL for liquids, 15g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510C (separatory funnel) or Method 3511 (microextraction). Solid samples are extracted with a hexane/acetone mixture using Method 3540 (Soxhlet), Method 3541 (Automated Soxhlet), Method 3546 (microwave), or Method 3550 (ultrasonic extraction). The extraction procedures use a hexane solvent exchange (if necessary) in preparation of the final extract for analysis by GC/ECD.

2.3 A variety of cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Suggested cleanups include alumina (Method 3610), Florisil (Method 3620), silica gel (Method 3630), gel permeation chromatography (Method 3640), and sulfur (Method 3660).

2.4 After cleanup, the extract is analyzed by injecting a 2.5µL sample into a gas chromatograph equipped with a narrow bore fused silica capillary column and electron capture detector (GC/ECD).

3) Definitions

3.1 GC/ECD = Gas Chromatograph / Electron Capture Detector

3.2 Organic Free Water: Deionized (DI) reagent water meeting purity characteristics of ASTM Type II laboratory distilled water (daily conductivity <1.0 umhos/cm). For additional purification before use, the DI water is passed through an activated carbon filter.

3.3 Laboratory Control Sample (LCS): A known matrix spiked with compound(s) representative of the target analytes.

3.4 Matrix: The component or substrate (e.g., surface water, groundwater, soil) that contains the analyte of interest.

3.5 Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis.

3.6 Matrix Spike Duplicate (MSD): A duplicate sample spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis.

3.7 Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure.

3.8 Standard Curve: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards that cover the working range of the instrument and are prepared at the frequency specified in the calibration section of the method.

3.9 Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.

3.10 NCR/CAR: Non-Conformance/Corrective Action Report (refer to SOP HN-QS-003, current revision)

4) Health and Safety Warnings

4.1 Lab Safety

4.1.1 Due to various hazards in the laboratory, safety glasses, disposable gloves, and laboratory coats or aprons must be worn when working with unknown samples. In addition, heavy-duty gloves and a face shield are recommended when dealing with toxic, caustic, and/or flammable chemicals.

4.1.2 The toxicity or carcinogenicity of each reagent used has not been precisely defined. However, each chemical used must be treated as a potential health hazard and exposure reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in

this method. A reference file of data handling sheets (SDS) is available to all personnel involved in these analyses.

4.2 Waste Disposal

4.2.1 Procedures for sample disposal are documented in SOP HN-SAF-001, *Waste Disposal Procedures*.

4.2.2 Samples must be disposed according to Federal, State, and local regulations.

4.3 Pollution Prevention

4.3.1 The quantities of chemicals purchased, when possible, must be based on the expected usage during its shelf life.

4.3.2 Standards and reagents must be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

5) Cautions

5.1 The electron capture detectors measure chlorinated compounds. Exposure of the detectors to extraneous chlorinated sources, such as methylene chloride, must be avoided.

5.2 Analysts should evaluate the specific toxaphene standard carefully. Some Toxaphene components, particularly the more heavily chlorinated components, are subject to dechlorination reactions. Therefore, standards from different vendors may exhibit marked differences that could lead to possible false negative results or to large differences in quantitative results.

5.3 Routine preventative maintenance must be performed as scheduled and documented to assure optimum instrument performance. Refer to SOP HN-EQ-004 for additional information.

5.4 An annual wipe test is conducted on the ECD detectors to indicate a failed detector that may be leaking radiation. Ensure that wipe tests are conducted for each detector, in a timely manner, once kits are received.

6) Interferences

6.1 Sources of interference in this method can be grouped into three general categories.

6.1.1 Contaminated solvents, reagents, or extraction apparatus.

6.1.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

6.1.3 Compounds extracted from the sample matrix to which the detector will respond.

6.2 Interferences co-extracted from the samples will vary considerably. While general cleanup techniques are referenced, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

6.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations.

6.3.1 These materials may be removed prior to analysis using Method 3640 (Gel Permeation Cleanup) or Method 3630 (Silica Gel Cleanup).

6.3.2 Common flexible plastics contain varying amounts of phthalate esters that are easily extracted or leached from such materials during laboratory operations.

6.3.3 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

6.3.4 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. The cleaning should include detergent washing with hot water, and rinses with tap water, and rinses with organic-free reagent water. Drain the glassware and dry it in an oven at 130°C for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

6.4 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Co-eluting organophosphorus pesticides may be eliminated utilizing Method 3640 (gel permeation cleanup - pesticide option). Co-eluting chlorophenols may be eliminated utilizing Method 3630 (silica gel), Method 3620 (florisil), or Method 3610 (alumina). Polychlorinated biphenyls (PCBs) also may interfere with the analysis of the organochlorine pesticides. The problem may be most severe for the analysis of multi-component analytes such as Chlordane and Toxaphene. If PCBs are known or expected to occur in samples, the analyst should consult Methods 3620 and 3630 for techniques that may be used to separate the pesticides from the PCBs.

7) Personnel Qualifications and Responsibilities

7.1 This method should be used by, or under the supervision of, analysts experienced in the use of solvent extraction and gas chromatography. The analysts should also be skilled in the interpretation of capillary gas chromatography, quantitation using computerized data, and use of peak processing software with baseline and peak grouping function.

7.2 Analyst - It is the responsibility of the analyst(s) to:

7.2.1 Produce contractually compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HN-QS-009).

7.2.2 Complete the required demonstration of proficiency before performing this procedure without supervision.

7.2.3 Create and populate a LIMS data entry batch for review by the Supervisor.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required demonstration of proficiency before performing this procedure without supervision.

7.3.3 Produce contractually compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to:

7.4.1 Ensure that all contractual requirements for a client requiring this procedure are understood prior to initiating this procedure for a given set of samples.

8) Sample Collection, Handling, and Preservation

8.1 Water samples are collected in 125mL glass jars with Teflon lined lids. Samples must be extracted within 7 days of collection and stored at 4 ± 2 °C until extraction.

8.2 Solid samples are collected in glass jars with Teflon lined lids. Solid samples must be extracted within 14 days of sample collection and stored at 4 ± 2 °C until extraction.

8.3 Sample extracts must be stored at 4 ± 2 °C, and must be analyzed within 40 days of the extraction date.

8.4 For aqueous samples collected from sources having residual chlorine present, preserve by addition of 3-ml of 10% sodium thiosulfate solution per gallon (or 0.008%). The addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use.

ORGANOCHLORINE PESTICIDES			
Sample Matrix	Container	Preservative	Holding Time
Concentrated Waste Samples	125-mL widemouth glass with Teflon lined lid.	None	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Aqueous Samples With No Residual Chlorine Present	3 x 125-mL, amber glass container with Teflon-lined lid.	Cool to 4°C	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Aqueous Samples WITH Residual Chlorine Present	3 x 125-mL, amber glass container with Teflon-lined lid.	Add 3-ml 10% NaS2O3 solution per gallon (0.008%). Cool to 4°C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Solid Samples (e.g. soils, sediments, sludges, ash)	4oz wide-mouth glass container with Teflon-lined lid	Cool to 4°C	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.

9) Equipment and Supplies

9.1 Gas chromatograph – A HP 7890 GC (or equivalent) equipped with electron capture detector(s) (ECD).

9.2 GC columns – The dual column approach involves a single injection that is split between two columns that are mounted by a Y-shaped fused silica connector in a single gas chromatograph. Recommended columns are:

9.2.1 30.0m x 0.32mm ID x 0.32um Rtx-CLPesticides (Restek cat.# 11141)
9.2.2 30.0m x 0.32mm ID x 0.25 um Rtx-CLPesticides (Restek cat.# 11324)
9.2.3 5m x 0.32mm ID Siltek Deactivated Guard Column (Restek cat. # 10027)

9.3 Syringes - 10ul, 0.1mL, 0.5ml & 1.0mL

9.4 Volumetric Flasks, class A, assorted sizes

10) Standards and Reagents

10.1 **Note:** Store the standard solutions (stock, composite, calibration and surrogate) at 0 to 6° C in Teflon™ sealed containers in the dark. All purchased stock standard solutions should be replaced after one year or sooner if routine QC tests indicate a problem. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem.

10.2 Solvents used in the extraction and cleanup procedures (appropriate 3500 and 3600 series methods) include n-hexane, methylene chloride, acetone and ethyl acetate and must be exchanged to n-hexane prior to analysis. Therefore, n-hexane is required in this procedure. Acetone or toluene may be required for the preparation of some standard solutions. All solvents must be pesticide quality or equivalent. Reagent grade or pesticide grade chemicals shall be used.

10.3 Stock standard solutions should be purchased as certified solutions. Two calibration mixtures are prepared for the single component analytes of this method. This procedure is used to minimize potential resolution and quantitation problems on confirmation columns and to allow determination of endrin and 4,4'-DDT breakdown for method QC. Separate single level calibration standards are prepared for each multi- component target analyte (e.g., Toxaphene and Chlordane).

10.4 Expiration dates of working standards must not exceed those of the parent standard(s).

10.5 Stock Pesticide Surrogate Mix @ 200 µg/ml (decachlorobiphenyl and 2,4,5,6 tetra chloro-meta-xylene), Ultra ISM-320 or equivalent

10.5.1 Pesticide Surrogate Spiking Mix @ 1 ug/ml:

10.5.1.1 Add 500 ul of the stock pesticide surrogate mix (Section 10.5) to approximately 90 ml of hexane in a 100 ml Class A volumetric flask.
10.5.1.2 Bring to volume with hexane and transfer to an appropriately labeled container.
10.5.1.3 This solution should be replaced every 6 months or if degradation is noted.
10.5.1.4 The expiration date of this solution may not exceed that of its parent stock.

10.6 Pesticide Calibration Mix @ 1000 ug/ml, Ultra Scientific #PPM-808C or equivalent

10.7 Pesticide Initial Calibration Intermediate Stock @ 10 ug/ml:

10.7.1 Add 500 ul of the pesticide calibration mix (Section 10.6) to approximately 40 ml of hexane in a 50 ml Class A volumetric flask.
10.7.2 Bring to final volume with hexane and transfer to an appropriately labeled container.
10.7.3 This solution should be replaced every 6 months or if degradation is noted.
10.7.4 The expiration date of this solution may not exceed that of any parent stock.

10.8 Pesticide Initial Calibration Working Stock @ 0.1 ug/ml:

10.8.1 Add 100 ul of the pesticide intermediate (Section 10.7) to approximately 8 ml of hexane in a 10 ml Class A volumetric flask.
10.8.2 Add 1000 ul of Pesticide Surrogate Spiking Mix (Section 10.5).
10.8.3 Bring to final volume with hexane and transfer to an appropriately labeled container.
10.8.4 This solution should be replaced every 6 months or if degradation is noted.
10.8.5 The expiration date of this solution may not exceed that of any parent stock.

10.9 Initial Calibration Standards:

10.9.1 Using an appropriate sized syringe, add the amounts as noted in Table 10.9 of initial calibration working stock (Section 10.8) and hexane to a 2 ml amber vial.
10.9.2 Prepare every 6 months or if degradation is noted.

	Table 10.9	Hexane (ul)	ICal Working Stock (ul)	Final Volume (ml)	Conc. (ug/ml)
1.	Level A	990	10	1	0.001
2.	Level B	980	20	1	0.002
3.	Level C	970	30	1	0.003
4.	Level D	950	50	1	0.005
5.	Level E	920	80	1	0.008
6.	Level F	900	100	1	0.010
7.	Level G	850	150	1	0.015
8.	Level H	800	200	1	0.020
9.	Level I	500	500	1	0.050

10.10 Organochlorine Pesticide Mix AB #1 @ 200 ug/ml, Restek #32291 or equivalent

10.11 Initial Calibration Verification Stock Standard @ 1.0 ug/ml

10.11.1 Add 50 ul of the stock pesticide surrogate mix (Section 10.5) to approximately 8 ml of hexane in a 10 ml Class A volumetric flask.
10.11.2 Add 50 ul of the pesticide mix AB #1 (Section 10.10).
10.11.3 Bring to final volume with hexane and transfer to an appropriately labeled container.
10.11.4 Replace every 6 months or if degradation is noted.
10.11.5 The expiration date may not exceed that of any parent stock.

10.12 Initial Calibration Verification Standard @ 0.01 ug/ml

10.12.1 Add 10 ul of ICV Stock Standard (Section 10.11) to a final volume of 1ml hexane.
10.12.2 Replace every 6 months or if degradation is noted.
10.12.3 The expiration date may not exceed that of any parent stock.

10.13 Stock Toxaphene Standard, 1000 µg/ml: Restek # 32005 or equivalent.

10.13.1 Toxaphene Initial Calibration Standard, 10 µg/ml : using the appropriate syringe, inject 100 µL of Stock Toxaphene (sec 10.13) into a 10 ml volumetric flask containing ~8 ml of pesticide grade n-hexane. Bring to volume and mix. Transfer to an amber glass bottle. Prepare fresh every 6 months.
10.13.2 Working Toxaphene Calibration Standards (Levels 1 through 6): using the appropriate syringe, inject noted volumes in Table 10.13.2 of Toxaphene Initial Calibration Standard (sec 10.13.1) and pesticide grade n-hexane into a 2ml clear vial.

	Table 10.13.2	Hexane (ul)	ICal Std (ul)	Final Volume (ml)	Conc. (ug/ml)
1.	Level A	990	10	1	0.1
2.	Level B	975	25	1	0.25
3.	Level C	950	50	1	0.50
4.	Level D	900	100	1	1.00
5.	Level E	750	250	1	2.50
6.	Level F	500	500	1	5.00

10.14 Stock Technical Chlordane, 1000 µg/ml: Restek # 32021 or equivalent.

10.14.1 T. Chlordane Initial Calibration Standard, 10 µg/ml: using the appropriate syringe, inject 100 µL of Stock Chlordane (sec 10.14) into a 10 ml volumetric flask containing ~8 ml of pesticide grade n-hexane. Bring to volume and mix. Transfer to a glass bottle. Prepare fresh every 6 months.

10.14.2 Working T. Chlordane Calibration Standards (Levels 1 through 6): using the appropriate syringe, inject noted volumes in Table 10.14.2 of T. Chlordane Initial Calibration Standard (sec 10.14.1) and pesticide grade n-hexane into a 2ml clear vial.

	Table 10.14.2	Hexane (ul)	ICal Stock (ul)	Final Volume (ml)	Conc. (ug/ml)
1.	Level A	990	10	1	0.10
2.	Level B	975	25	1	0.25
3.	Level C	950	50	1	0.50
4.	Level D	900	100	1	1.00
5.	Level E	750	250	1	2.50
6.	Level F	500	500	1	5.00

10.15 Degradation Check Solution (4,4'-DDT and Endrin @ various concentrations): Ultra ISM-450 or equivalent.

10.15.1 Add 1000 ul of the degradation check solution (Section 10.15) to approximately 8 ml of hexane in a 10 ml Class A volumetric flask.
10.15.2 Bring to final volume with hexane and transfer to an appropriately labeled container.
10.15.3 This solution should be replaced every 6 months or if degradation is noted.
10.15.4 The expiration date of this solution may not exceed that of any parent stock.

11) Method Calibration

11.1 Analytical Conditions: The dual-column approach involves the use of two fused-silica open-tubular columns of different polarities, thus, different selectivity towards the target analytes. The columns are connected to an injection tee and separate electron-capture detectors or utilized separately (dependent upon GC setup). Recommended operating conditions are:

GC Operating Conditions		
GC Conditions	Column 1	Column 2
Carrier gas:	Helium	Helium
Carrier gas flow rate:	2.808ml/minute @120°C (Constant)	1.7ml/minute @120°C (Constant)
Head pressure:	16 psi	10.895 psi
Makeup gas:	Nitrogen	Nitrogen
Makeup gas flow rate:	60ml/minute	60ml/minute
Injector temperature:	250°C	250°C
Detector temperatures:	330°C	330°C
Temperature program:	120 °C for 0.3 min, 120°c to 200°C at 45°C/min, to 230°C at 10°C/min, to 320°C at 25°C/min and hold for 2 min.	120 °C for 0.3 min, 120°c to 200°C at 45°C/min, to 230°C at 10°C/min, to 320°C at 25°C/min and hold for 2 min.

Note: Once optimized and calibrated, the same GC conditions must be used for analysis of all standards, samples, blanks and QC samples (LCS/MS/MSD).

11.2 Initial Calibration Curve: External standard calibration should be used due to the sensitivity of the electron capture detector and the probability of the internal standard being affected by interferences. Because several of the pesticides may co-elute on any single-column, analysts use two calibration mixtures. Because of the sensitivity of the electron capture detector, the injection port and column must always be cleaned prior to performing the initial calibration. A 5-point (minimum) calibration curve is required for all analytes.

11.2.1 A 2.5µL injection volume of each calibration standard is used. Other injection volumes may be employed, if sensitivity for the compounds of interest is adequate.
11.2.2 GC Column Deactivation: Low concentrations of pesticide standards injected on a GC/ECD column may result in adsorption when the GC has not been in continuous use (several days or more). To deactivate the

potential column adsorption, the GC column should be primed (or deactivated) by injecting a pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

11.3 Calibration Factors for Initial Calibration

For the initial curve generation, calculate the calibration factor for each analyte at each standard concentration. Calculate the mean calibration factor, and the relative standard deviation (RSD) of the calibration factors, using pertinent formula listed below. The calculation for the calibration factor and corresponding RSD for each analyte is described in section 15.

11.3.1 If the RSD for each analyte is < 20%, then the response of the instrument is considered linear and the mean calibration factor can be used to quantitate sample results. If the RSD is greater than 20%, then linearity through the origin cannot be assumed. The analyst must use a calibration curve or a non-linear calibration model (e.g., a polynomial equation) for quantitation.

11.3.2 For a linear calibration curve ($y = ax + b$), the analyst shall not force the line through the origin, but leave the intercept calculated. In addition, do not include the origin (0,0) as a calibration point. In order to be used for quantitative purposes, a correlation coefficient must be greater than or equal to 0.995.

11.3.3 When the other approaches described above have not met the acceptance criteria, a non-linear calibration model may be employed. A quadratic (second order) model requires a minimum of six standards.

11.3.3.1 $Y = ax^2+bx+c$

11.3.3.2 In order to be an acceptable non-linear calibration, the coefficient of the determination (COD) must be greater than or equal to 0.995.

11.3.4 Retention time window:

11.3.4.1 Record the retention time for each analyte in each calibration standard

11.3.4.2 Calculate the mean retention time for each analyte and the standard deviation (SD)

11.3.4.3 Set the retention time window for each analyte to the mean value $\pm$ 3 times the SD

11.3.4.4 If the SD of the analyte is 0.000 (no difference between analyses), use a default SD of 0.01 minutes

11.3.4.5 Retention time windows must be established for each instrument and for analytical modifications.

11.3.4.6 If the instrument software cannot process analyte specific retention time windows, the analyst may choose the widest window and apply it to all analytes.

11.4 Initial Calibration Verification

11.4.1 Verify each new Initial Calibration using a second source standard at or near the midpoint of the curve. Agreement with the new curve must be ± 20 percent of the true value of the second source standard.

11.5 Continuing Calibration Verification

11.5.1 Verify calibration by injecting calibration verification standards prior to sample analyses, after every 10 samples, and at the end of the sequence.

11.5.2 Instrument blanks may not be used prior to a CCV for the purpose of achieving acceptance criteria (see Section 12.6).

11.5.3 Due to the instability and potential drift of the ECD, the analyst should alternate the mid-level CCV with the high and low-level CCVs.

11.5.4 The calibration for each analyte shall not exceed a ± 20 percent difference from the mean calibration factor calculated for the initial calibration.

11.5.5 If the calibration does not meet the ±20% limit, check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±20%, then a new initial calibration must be prepared.

11.5.6 Compare the retention time of each analyte in the calibration standard with the established retention time window. Each analyte must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard does result in all analytes falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established.

11.6 Degradation Check

11.6.1 Pesticide breakdown (degradation) must be verified prior to sample analysis or once every 12 hours whichever is less by injecting 1 ul of the pesticide degradation check solution (Section 10.1.4.1).

11.6.2 The presence of 4,4'-DDE, 4,4'-DDD, endrin ketone, or endrin indicates breakdown.

11.6.3 Degradation of DDT or endrin must be $\leq$ 15% prior to sample analysis.

11.6.4 Caluclate breakdown percentage as follows:

$$\%\ \text{DDT Breakdown} = \frac{\text{Sum of degradation areas (DDD + DDE) X 100}}{\text{Sum of all areas (DDT+DDE+DDD)}}$$

$$\%\ \text{Endrin Breakdown} = \frac{\text{Sum of degradation areas (aldehyde + ketone) X 100}}{\text{Sum of all areas (Endrin + aldehyde + ketone)}}$$

12) Sample Preparation/Analysis

12.1 Sample Preparation

12.1.1 Water samples are extracted utilizing SW 3510C (SOP HN-EXT-001) or SW 3511 (SOP HN-EXT-011) .

12.1.2 Soil samples are extracted utilizing SW 3541 (SOP HN-EXT 003), SW 3546 (SOP HN-EXT-016), or SW 3550C (SOP HN-EXT-013).

12.2 Gas chromatographic analysis of sample extracts

12.2.1 Inject a 2.5µL aliquot of the concentrated sample extract.

12.2.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the absolute retention time window. Tentative identifications must be confirmed using either a second GC column of dissimilar stationary phase or a dissimilar detector.

12.2.3 When results are confirmed, the analyst should check the agreement between the quantitative confirmations. Unless otherwise specified in an approved project plan, the higher result should be reported, as this is a conservative approach relative to protection of the environment. Calculate the relative percent difference of the results using the formula below.

12.2.3.1 $RPD = (([R_1 - R_2]) / ((R_1 + R_2) / 2)) \times 100$

12.2.4 If one column result is significantly higher (>40%), check the chromatograms to see if an obvious overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established during peak integration. If no anomalies are noted, review the chromatographic conditions. If there is no evidence of a chromatographic problem, report the higher result. The data user must be advised of the disparity between the results on the two columns (LIMS will place a data flag).

12.3 Calculate constituent concentration as specified in Section 15.

12.4 The MQL must be at or above the lowest level of calibration.

12.5 If the responses exceed the calibration range of the system, the extract must be diluted and reanalyzed.

12.6 If instrument blanks are utilized to maintain system cleanliness, blank injections must be maintained on a consistent basis (i.e., after every sample, every 5 samples, etc).

12.7 Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

12.8 Each sample analysis must be bracketed with acceptable calibration verification standards (minimum every 20 sample injections).

12.9 The results from these bracketing standards must meet the calibration verification criteria of +/- 20%. When calibration verification standards fail to meet QC criteria, all samples that were injected after the last acceptable standard must be re-analyzed and/or evaluated to prevent improper reporting. More frequent analysis of standards will minimize the number of sample extracts that require such action if the QC limits are violated for the standard analysis.

Note: If the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit (i.e., >20%) and the analyte was not detected in the applicable samples, the extracts for those samples do not need to be reanalyzed.

12.10 Sample injections may continue for as long as the calibration verification standards (and standards interspersed with the samples) meet instrument QC requirements.

12.11 Use the calibration standards analyzed during the sequence to evaluate retention time stability. Each injection of a standard during the analytical run (i.e., those standards injected every 20 samples, or more frequently) must be checked against the retention time windows. If any of these subsequent standards fall outside their absolute retention time windows, determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

12.12 Identification of mixtures (i.e. Chlordane and Toxaphene) is based on the characteristic "fingerprint" retention time and shape of the indicator peak(s); and quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peak(s) of the same retention time and shape generated using either internal or external calibration procedures.

12.13 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector may be warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix.

12.14 Quantitation of Toxaphene: Toxaphene is manufactured by the chlorination of camphenes. Quantitation of Toxaphene is difficult, but reasonable accuracy can be obtained. To calculate Toxaphene from GC/ECD results:

12.14.1 Inject a Toxaphene standard that is estimated to be within ± 10 ng of the sample amount.

12.14.2 Quantitate Toxaphene using the total area of the Toxaphene pattern or using 4 to 6 major peaks. While Toxaphene contains a large number of compounds that will produce well-resolved peaks in a GC/ECD chromatogram, it also contains many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of this mixture. Although the resolved peaks are important for the identification of the mixture, the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

12.14.3 Toxaphene may also be quantitated based on 4 to 6 major peaks. When Toxaphene is determined using the 4 to 6 peaks approach, the analyst must take care to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms. It is highly unlikely that the peaks will match exactly, but the analyst should not employ peaks from the sample chromatogram whose relative sizes or areas appear to be disproportionately larger or smaller in the sample compared to the standard. The heights or areas of the 4 to 6 peaks should be summed together and used to determine the Toxaphene concentration. Alternatively, use each peak in the standard to calculate a calibration factor for that peak, using the total mass of Toxaphene in the standard. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 4 to 6 resulting concentrations are averaged to provide the result for the sample. Chlordane - Technical Chlordane is a mixture of at least 11

major components and 30 or minor components that is used to prepare specific pesticide formulations. The CAS Registry number for Technical Chlordane is properly given as 12789-03-6. *Trans*-Chlordane (or α-Chlordane, CAS RN 5103-71-9)and *cis*-Chlordane (γ-Chlordane, CAS RN 5103-74-2), are the two most prevalent major components of Technical Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch. Moreover, changes may occur when the technical material is used to prepare specific pesticide formulations. The approach used for evaluating and reporting Chlordane results will often depend on the end use of the results and the analyst's skill in interpreting this multi-component pesticide residue. The following sections discuss three specific options: reporting Technical Chlordane (12789-03-6), reporting Chlordane (not otherwise specified, 57-74-9), and reporting the individual Chlordane components that can be identified under their individual CAS numbers.

12.14.4 When the GC pattern of the residue resembles that of Technical Chlordane, the analyst may quantitate Chlordane residues by comparing the total area of the Chlordane chromatogram using three to five major peaks or the total area. If the Heptachlor epoxide peak is relatively small, include it as part of the total Chlordane area for calculation of the residue. If Heptachlor and/or Heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected Chlordane area.
(NOTE: Octachloroepoxide, a metabolite of Chlordane, can easily be mistaken for Heptachlor epoxide on a nonpolar GC column.)

12.14.5 To measure the total area of the Chlordane chromatogram, inject an amount of a Technical Chlordane standard that will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms. Construct the baseline of Technical Chlordane in the standard chromatogram between the retention times of the first and last eluting Chlordane components. Use this area and the mass of Technical Chlordane in the standard to calculate a calibration factor. Construct a similar baseline in the sample chromatogram, measure the area, and use the calibration factor to calculate the concentration in the sample.

12.14.6 The GC pattern of a Chlordane residue in a sample may differ considerably from that of the Technical Chlordane standard. In such instances, it may not be practical to relate a sample chromatogram back to the pesticide active ingredient Technical Chlordane. Therefore, depending on the objectives of the analysis, the analyst may choose to report the sum of all the identifiable Chlordane components as "Chlordane (n.o.s.)" under the CAS #57-74-9.

12.14.7 The third option is to quantitate the peaks of α-Chlordane, γ-Chlordane, and Heptachlor separately against the appropriate reference materials, and report these individual components under their respective CAS numbers. To measure the total area of the Chlordane chromatogram, inject an amount of a Technical Chlordane standard that will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

13) Troubleshooting

13.1 Refer to HP 7890 GC hardware manual for specific technical guidance.

14) Data Acquisition

14.1 Dependent upon instrument setup, data is collected with the ChemStation data acquisition software. This software provides the sequence log of run order for the data to be collected from the ECD detectors and the associated signal response.

14.2 The data processing software processes the calibration curve and all associated sample and QC data.

14.3 LIMS receives the processed data in its data entry module and links the data to the samples in a specific work order. The QC batch data is also linked to the data.

15) Calculation, and Data Reduction Requirements

15.1 Calibration Factor (CF) and calibration RSD calculations:

15.1.1 Calibration Factor for each analyte at each concentration, calculate using:

15.1.1.1 $$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

15.1.1.2 $$Mean\ CF = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where: n is the number of standards analyzed.

15.1.2 Calculate the standard deviation (SD) and the RSD of the calibration factors for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \times 100$$

15.2 Calculation of Linear Regression Correlation Coefficient, r

$$r = \frac{\sum XY - \frac{\sum X \sum Y}{n}}{\sqrt{\left(\sum X^2 - \frac{(\sum X)^2}{n}\right)\left(\sum Y^2 - \frac{(\sum Y)^2}{n}\right)}}$$

Where:

X = individual values for independent variable
Y = individual values for dependent variable
n = number of pairs of data.
df = n-2

15.3 Calculation of % drift by using the following formula:

15.3.1 % Drift= [(Calculated conc - Theoretical conc) x 100] / Theoretical conc

15.4 Calculation of % difference (using the calibration factors):

15.4.1 % Difference = [(CF - mean CF) x 100] / mean CF

where:

CF = the calibration factor from the CCV and
mean CF = the mean calibration factor from the initial calibration

15.5 Dual Column Confirmation RPD: When results are confirmed using a second GC column of dissimilar stationary phase, calculate the relative percent difference of the results using the formula below.

15.5.1 $RPD = ([R_1-R_2] / ((R_1+R_2)/2)) * 100$

where R_1 and R_2 are the results on the two columns.

15.6 Sample Quantitation using External calibration:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(Wt)}$$

A_x = Concentration of the analyte in the sample.
V_t = Total volume of the concentrated extract.
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.
Wt = Volume or mass of sample extracted

15.6.1 The wet weight or dry weight may be used, depending upon the specific application of the data.

15.7 QC Calculations: Calculate the percent recovery for surrogates and for various QC samples (MS, MSD, LCS) according to the following equations:

15.7.1 Surrogate Recovery: Sample, matrix spike/matrix spike duplicate, duplicate, and blank samples are all spiked with surrogates prior to purging. Surrogate percent recovery is calculated as follows:

$$\% R = \frac{(SurrSR)}{SurrSA} \times 100$$

Where:

SurrSR = Surrogate Spiked Sample Result (mg/L or mg/kg).
SurrSA = Surrogate Spike Amount Added (mg/L or mg/kg).

15.7.2 % Recovery, %R (MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:

SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.7.3 % Recovery, %R (Standards, LCS)

$$\% R = \frac{(SSR)}{SA} \times 100$$

Where:

SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.7.4 % RPD (for precision or replication evaluation)

$$\%RPD = \frac{|SR_1 - SR_2|}{\frac{1}{2}(SR_1 + SR_2)} \times 100$$

Where:

SR_1 = Sample result for replicate 1.
SR_2 = Sample result for replicate 2.

16) Quality Control, Data Assessment and Corrective Action

16.1 Pesticide Degradation

16.1.1 Frequency

16.1.1.1 Pesticide degradation must be verified prior to sample analysis or every 12 hours whichever occurs first.

16.1.2 Acceptance Criteria

16.1.2.1 Degradation of DDT and Endrin must each be ≤ 15%.

16.1.3 Corrective Action

16.1.3.1 Perform injector and/or column maintenance.
16.1.3.2 All analysis associated with a failed degradation check must be re-analyzed.

16.2 Initial Calibration:

16.2.1 Frequency: A new curve must be generated after changes in operating conditions, after major instrument maintenance, and/or upon failure of the ICV or CCV to achieve acceptance criteria.
16.2.2 The lowest level calibration must be at or below the MQL.
16.2.3 Acceptance Criteria:

16.2.3.1 Initial calibration curve must contain 5-points minimally for all analytes;
16.2.3.2 The mean RSD for all analytes must be $\leq$ 20 % *or* perform the least squares regression (r >0.995) for analytes.
16.2.3.3 If non-linear fit (second order) is used, the COD > 0.995 and six calibration points are required.

16.2.4 Curve Failure Corrective Action:

16.2.4.1 Check standards and or perform maintenance as necessary to correct problem, then generate new curve

16.3 Initial Calibration Verification (ICV):

16.3.1 Frequency: Perform this evaluation each time a new curve is generated.
16.3.2 Acceptance criteria:

16.3.2.1 Agreement between the curve and the ICV results must meet accuracy performance criteria of $\pm$20% from the known value.

16.3.3 ICV Failure Corrective action:

16.3.3.1 Evaluate condition and age of standards being used and repeat analysis
16.3.3.2 Do not analyze samples until the criteria can be met or prepare new standards and /or generate new curve if criteria cannot be met.

16.4 Continuing Calibration Verification (CCV):

16.4.1 Frequency:

16.4.1.1 The calibration standard must be run at the beginning of each daily batch,
16.4.1.2 After every 10 samples (including QC samples)
16.4.1.3 At the end of the analytical sequence.

16.4.2 Acceptance Criteria:

16.4.2.1 All analytes must meet accuracy performance criteria of ±20% from the known value.

16.4.3 Corrective Action:

16.4.3.1 If the calibration does not meet the criteria, correct the problem and re-analyze the standard or perform a new initial calibration.
16.4.3.2 All samples run since last passing CCV must be re-run.

16.5 Retention Time (RT) Window:

16.5.1 Frequency:

16.5.1.1 Calculate new RT windows with each new calibration curve.

16.5.2 Acceptance Criteria:

16.5.2.1 Set RT at ±3 times the SD around the mean for each analyte.
16.5.2.2 The ICV and CCVs must fall within the RT windows.

16.5.3 Corrective Action:

16.5.3.1 Correct problem then repeat the initial calibration

16.6 Method Blank:

16.6.1 Frequency:

16.6.1.1 Analyze the method blank at a frequency of one per preparation batch of 20 or less samples. If the method blank indicates contamination, it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

16.6.2 Acceptance Criteria:

16.6.2.1 All analytes of interest should be less than < ½ the MQL and must be less than the MQL.
16.6.2.2 All analytes of interest must < MQL.
16.6.2.3 Other approved QA program requirements must be followed when the acceptable blank contamination specified in the approved quality assurance project plan differs from the above.

16.6.3 Corrective Action:

16.6.3.1 If the method blank results do not meet the acceptance criteria above, then the laboratory must take corrective action to locate and